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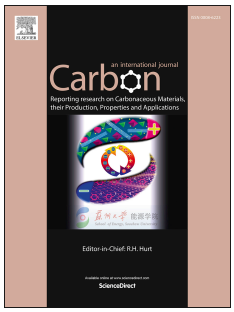

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Mesophase pitch-derived graphite foams with selective distribution of TiC nanoparticles for catalytic applications

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Abstract

TiC-supported metals are systems of great importance in catalysis science and technology. Albeit their interest, catalysts based on monoliths consisting of TiC-containing carbonaceous foams have not yet been fabricated. This work aims to present a route for fabrication of mesophase pitch-derived open-pore graphite foams with TiC nanoparticles selectively distributed in two locations: at the surface of the pore cells, able for metal-support, and in the bulk, essential to achieve high degree of graphitization for enhancement of thermal conductivity. The double distinctive effect of the nanoparticles in the monoliths makes these materials interesting to be checked in catalytic applications.

Titanium carbide (TiC) and other simple transition metal carbides are considered to be excellent supports for metallic nanoparticles able to act as catalysts in different reactions of technological importance such as molecular dissociation of oxygen and hydrogen, desulfurization, hydrogenation of CO_2 to methanol and the water-gas shift reaction, among others [1]. Fundamental insight into key features that influence the activity, selectivity, and lifetime of these nanocatalysts is nowadays under development. In spite of its current importance, there has been yet no attempt to fabricate porous TiC-containing ceramic monoliths for those catalytic applications. In the present contribution the author presents a fabrication route to obtain mesophase pitch-derived open-pore graphite foams with TiC nanoparticles selective distributed in two locations. A fraction ~~od~~ of particles is located in the bulk of the foam structure and serves to catalyse the conversion of the mesophase pitch into graphite, in order to increase the thermal conductivity of the foam (something that insures that the heat of any reaction is properly lead off from or supplied to the reactor). Another fraction of particles is at the surface of the pore cells and can serve as support for transition metallic nanoparticles for catalytic purposes.

Fabrication of the carbonaceous foams was achieved by the replication process [2]. Slight variations to the process presented in [2] were introduced in order to incorporate the TiC nanoparticles. In general terms, the process consists of infiltrating a liquid mesophase pitch (graphite precursor) doped with TiC nanoparticles into preforms of packed particles of NaCl supporting TiC nanoparticles on its surface. The

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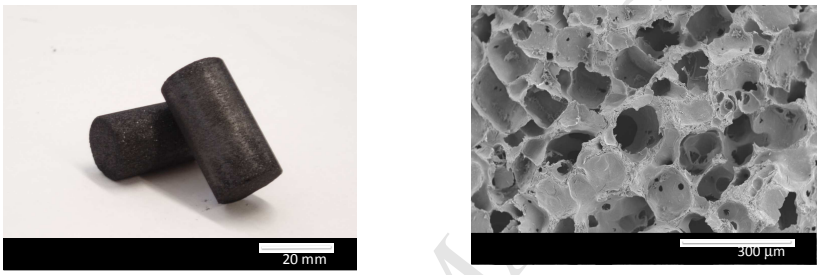
NaCl particles are afterwards leached by water dissolution and the mesophase-pitch foams are subsequently subjected to stabilization at 170 ºC under air atmosphere for 40 hours, carbonization at 1450 ºC under Ar gas flow using the following thermal profile: room temperature to 450 °C at 2 °C/min, 450–1450 °C at 4 °C/min and 1450–25 °C at 4 °C/min and graphitization at 2500 ºC or 2750 ºC under inert Ar atmosphere for 30 minutes each.

NaCl particles of analytical quality (99.5 % purity) were purchased from Sigma-Aldrich (Riedstr, Switzerland). These particles, originally of 30-400 μm, were grinded and sieved in order to obtain fractions of narrower particle size distributions from which those in the range 100-150 μm were selected. TIC nanoparticles were purchased from Sigma-Aldrich (Riedsth, Switzerland) as titanium (IV) carbide (TiC) nanopowder <200nm of high purity (>95%), with a nominal specific surface of 19 m^2/g (provided by the supplier). The graphite precursor was the Mistsubishi AR24 naphthalene-based synthetic mesophase pitch, kindly supplied as pellets by Mitsubishi Gas Chemical Company Inc. (Tokyo, Japan).

Doping of mesophase pitch with TiC nanoparticles was achieved by dispersion with toluene following the next procedure: i) TiC nanoparticles are mixed with the mesophase pitch in desired proportions in a reactor flask; ii) toluene is added in 25:75 weight proportion of mesophase pitch:toluene; iii) the mixture is homogenized by a mechanical blade-stirring system for 1h: iv) ultrasounds are applied to the reactor during 1h; and v) toluene is evaporated by magnetic stirring until dried mixture is attained. In order to obtain a complete toluene-free mixture, an extra final step is added: the TiC-doped mesophase pitch is molten and mechanically blade-stirred during 1h, after which it is solidified and subsequently ball milled.

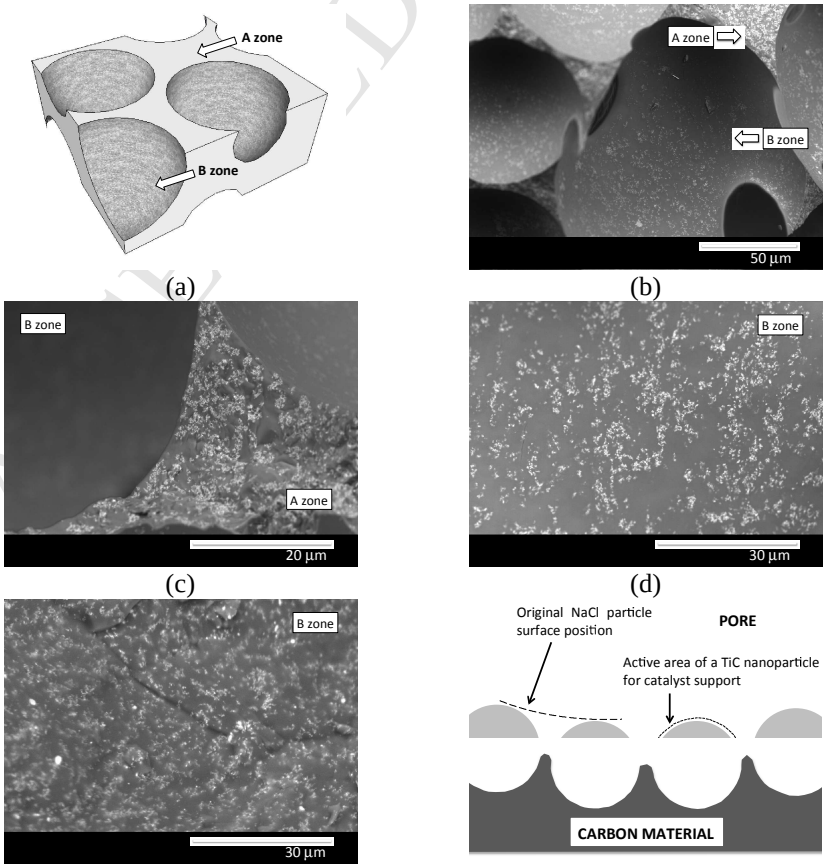
TiC nanoparticles supported on the NaCl particles were prepared by mechanically mixing the right proportion of TiC and NaCl ~~both types of~~ particles during 30 minutes. The TiC nanoparticles stuck to the surface of NaCl by ~~inter~~particle interactions (mainly of electrostatic nature) generated during the mechanical mixing. The TiC-NaCl particulate system was delicately packed in glass containers consisting of tubes (17 mm inner diameter) closed on one side and afterwards ~~. The volume fraction attained was 0.56 ± 0.01. Careful optical microscopy images of the packed preforms revealed that no particle breaking occurred during packing. These packings were~~ infiltrated with the TiC-doped mesophase pitch at a temperature of 300ºC and pressure of 0.5 MPa (for infiltration and subsequent dissolution of NaCl particles please see [2]). Immediately after infiltration the mesophase pitch was rapidly solidified in less than 5 seconds by immersing the infiltration chamber into a cold-water bath. Characterization of the monoliths was carried out by different techniques. Fracture surfaces were ~~observed~~ examined under

electron microscopy and both the total pore volume fraction and the content of TiC particles in different zones of the foams were analysed with Buehler-Omnimet Enterprise (Illinois, USA) analysis software. Helium pycnometry was applied to the fabricated materials in two conditions: as obtained (foam state) and after milling (powder state). In combination with the total pore volume fraction obtained by image analysis, it allowed deriving the open and closed porosity of the final materials. ~~Their~~ The thermal conductivity was obtained by averaging over six independent measurements from three different samples fabricated at same exact conditions ~~measured~~ by means of a relative steady-state technique in an experimental setup assembled in the laboratories of Alicante University by following the ASTM E-1225-04 International Standard (the relative error is 5%). Additionally, the total specific surface was determined by nitrogen adsorption technique and the Brunnauer, Emmet and Teller (BET) method.



(a) (b)

Figure 1. Images of mesophase pitch-derived graphite foams with selective distribution of TiC nanoparticles: (a) photograph of cylindrical samples; (b) SEM image of the fracture surface.



(a) (b) (c) (d)

(e) (f)

Figure 2. Schematic drawings (a and f) and SEM images (b-e) showing the location of TiC nanoparticles in the bulk (A zones) and at the pore cell surfaces (B zones) of mesophase pitch-derived foams. (b-d) correspond to sample G1-15-15 while (e) corresponds to sample G1-15-45. (f) is a representation of TiC nanoparticles at the pore cell surface, which are not completely embedded in the carbon material.

Figure 1 displays images of TiC-containing monoliths of open-pore graphite foams. ~~of cylindrical geometry and dimensions of approximately 17 mm diameter and 40 mm length.~~ Figure 1a is a photograph at an eye-view scale while Figure 1b is a micrograph of the foam structure at low magnification where the closely regular size and shape of the pore cells can be distinguished. More details of the complex microstructure of the TiC-containing graphite foams need to be observed at a higher magnification (Figure 2). Two main issues are distinguished: the pore cells and the solid struts, both containing TiC nanoparticles and named as B and A zones, respectively (please see the schematic drawing of Figure 2a and the micrograph in Figure 2b). Figure 2c is a magnification of a strut (A zone) where TiC nanoparticles can be distinguished. They appear to be well dispersed, although a close look reveals regions where local agglomeration is present. Figure 2d and Figure 2e correspond to micrographs of B zones of pore cells superficially doped with 15% and 45% of TiC nanoparticles, respectively (see sample codes and Table 1). In both cases TiC nanoparticles are nicely distributed and the dispersion structure seems adequate for catalytic purposes.

Table 1. Properties of different TiC_{bulk}-$TiC_{surface}$-doped carbon and graphite foams fabricated in the present work. Legend for the HTC (heat treatment condition): S - stabilized (pitch foam); C - carbonized at 1450ºC during 12h; G1 - graphitized at 2500ºC during 2h; G2 - graphitized at 2750ºC during 30 min. O and C refer to open and close porosity, respectively.

Sample code	HTC	Porosity (%)		TiC_{bulk} – A zone (%)		$TiC_{surface}$ – B zone (%)		BET (m^2/g)	TC (W/mK)
		O	C	nominal	measured	nominal	measured		
P-0-0	S	56.0	0.0	0	0.0	0	0.0	0.44	2.1
C-0-0	C	56.5	0.0	0	0.0	0	0.0	0.51	4.8
G1-0-0	G1	55.8	0.0	0	0.0	0	0.0	0.52	23
G1-0-15	G1	56.2	0.0	0	0.0	15	14.9	0.67	20
G1-0-45	G1	56.6	0.1	0	0.0	45	43.3	1.02	24
G1-5-0	G1	57.0	0.1	5	5.0	0	0.0	0.53	37
G1-5-15	G1	57.1	0.0	5	4.7	15	15.1	0.69	38
G1-5-45	G1	56.6	0.1	5	4.7	45	42.6	1.04	33
G1-15-0	G1	55.9	0.0	15	13.9	0	0.0	0.58	41
G1-15-15	G1	55.8	0.0	15	14.4	15	14.0	0.66	43
G1-15-45	G1	56.1	0.0	15	14.0	45	41.2	0.96	44
G2-0-0	G2	55.9	0.1	0	0.0	0	0.0	0.53	51
G2-15-45	G2	55.8	0.0	15	14.2	45	44.7	1.09	61

The properties of the foams fabricated in this work are gathered in Table 1. While specific comments on every sample must be sustained by a deeper careful characterization, two general trends of interest are worth mentioning. On the one hand, the samples containing TiC nanoparticles in the bulk (A zones) do show high values of thermal conductivity (the higher the TiC content the greater the TC of the foam).

This is as to be expected, since TiC nanoparticles were proved to favour the graphitization process and hence increase the thermal conductivity in carbon-carbon composites [3]. On the other hand, the presence of TiC nanoparticles at the pore cell surfaces (B zones) does not significantly modify the thermal conductivity of the foams (since they are not implied in the graphitization process). However, the higher the content of TiC nanoparticles in B zones the higher the specific surface of the foam, as measured by nitrogen adsorption (Table 1). The reason for this is that, due to the characteristics of the system and the fabrication process, the nanoparticles are only partially embedded in the mesophase pitch when infiltration takes place (Figure 2f). Reliable data on the wetting behaviour of the AR mesophase pitch are scarce and there is yet no study on TiC substrates; equilibrium contact angles of the AR mesophase pitch at 325 ºC on a variety of ceramic substrates are in between 30º and 45º [4]. It has been found that up to roughly 300ºC (the temperature used in present experiments) wetting spreading kinetics are very limited due to the fact that viscous dissipation is much important than surface tension driven flow for the movement of the triple line. Upon this scenario, and given the low infiltration pressures applied and that the presence of TiC nanoparticles increases the viscosity of the AR mesophase pitch, it can be expected that the kinetics of the present (rapid) infiltrations are much greater than the kinetics of pitch spreading on the TiC nanoparticles surface and, in consequence, the particles are not fully embedded in the liquid mesophase pitch (Figure 2f).

In conclusion, this work presents a route for the fabrication of mesophase pitch-derived open-pore graphite foams with TiC nanoparticles conveniently distributed in two locations: at pore cell surfaces and in the bulk material. TiC nanoparticles accomplish two different roles: those in bulk catalyse the graphitization process of the porous material while those at pore cell surfaces are able to actuate as metal supports for catalytic purposes. The most interesting materials are those graphitized at 2750ºC with 15% TiC in bulk and a pore cell coverage of 45% TiC, given their great thermal conductivity (61 W/mK) and relatively high specific area (1.09 m^2/g).

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